

Observations of the D/H ratio in Methane in the atmosphere of Saturn's moon, Titan - where did the Saturnian system form?

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Summary: The details of the Solar system's formation are still heavily debated. Questions remain about the formation locations of the giant planets, and the degree to which volatile material was mixed throughout the proto-planetary system. One diagnostic which offers great promise in helping to unravel the history of planet formation is the study of the level of deuteration in various Solar system bodies. For example, the D/H ratio of methane in the atmosphere of Titan can be used as a diagnostic of the initial conditions of the solar nebula within the region of giant planet formation, and can help us to determine where Titan (and, by extension, the Saturnian system) accreted its volatile material. The level of Titanian deuteration also has implications for both the sources and long term evolution of Titan's atmospheric composition. We present the results of observations taken in the $1.58\ \mu\text{m}$ window using the NIFS spectrometer on the Gemini telescope, and model our data using the VSTAR line-by-line transfer model, which yields a D/H ratio for Titan's atmosphere of $(143 \pm 16) \times 10^{-6}$ [1]. We are currently in the process of modeling the Gemini high resolution GNIRS spectra using new sets of line parameters derived for methane in the region between $1.2\text{-}1.7\ \mu\text{m}$ [2].

Keywords: Titan, methane, spectroscopy, radiative transfer, deuterium, planetary formation

Introduction

Over the years, our understanding of the formation of our Solar system has evolved dramatically. For a long time, it was believed that our planetary system was formed by a chance encounter between the Sun and another star, which passed sufficiently close to the Sun to draw a lengthy tongue of material from it which then coalesced to form the planets (e.g. [3, 4]). In recent decades, it has become widely accepted that our planetary system instead formed from a dynamically cold disk¹ of dust and gas around the proto-Sun. By the early 1990s, it was thought that the process of planetary formation was essentially a leisurely, gentle process that occurred at a fixed location within the proto-planetary disk (e.g. [5]).

It was soon realised that the planet formation process must be somewhat more complicated, involving proto-planets and planets migrating over many astronomical units from their formation location to their current locations. This sea-change in our understanding of planet

¹Objects moving on dynamically cold orbits have very low orbital eccentricity and inclination. Therefore a dynamically cold disk is rather flattened and consists of the protoplanetary material in orbits of very low eccentricity. Objects in dynamically cold orbits typically only experience collisions at very low relative velocities. Such collisions tend to be constructive rather than destructive.

formation came about, in part, as a result of the discovery of the first planets found around Sun-like stars (e.g. [6]), which were found moving on totally unexpected orbits (Jupiter-size planets orbiting far closer to their host stars than Mercury to our Sun). Within our own Solar system, planet formation models featuring migration were found to be necessary in order to explain various aspects of the distribution of small bodies in the outer Solar system including the orbits of Pluto and the Plutinos (e.g. [7, 8]), the proposed Late Heavy Bombardment of the inner Solar system (e.g. [9]) and the populations of Jovian and Neptunian Trojans (e.g. [10, 11]).

Although it is now widely accepted that the giant planets migrated significant distances before reaching their current locations, the nature, range, and pace of that migration are still heavily debated. Some models suggest a relatively sedate migration for the giant planets (e.g. [12]), whilst others suggest highly chaotic migration featuring significant mutual scattering between the giant planets (e.g. [13]). Whilst it is likely that dynamical studies of the small body populations in the outer Solar system may help to resolve the unanswered question of the nature of planetary migration (e.g. [14, 15]), the observation of isotopic abundances in the ices and atmospheres of objects in the outer Solar system will provide an important independent test of their formation locations (e.g. [16, 17]). In particular, the study of the deuterium-to-hydrogen (D/H) ratio in the icy and gaseous material in the outer Solar system may well provide a signpost to the formation location of the bodies in question.

In this work, we present the first results of an observational program targeted at determining the D/H ratio within methane in the atmosphere of Saturn’s largest satellite, Titan. In the next section, we describe in more detail the current state of play in our understanding of the way in which the D/H ratio varied through the proto-planetary disk, before briefly discussing the origin of methane in Titan’s atmosphere in the following section. Next we detail our observations of Titan and describe our modelling of the Titanian spectrum. Finally, we present our conclusions and discuss future work.

Deuterium and the formation of the Solar system

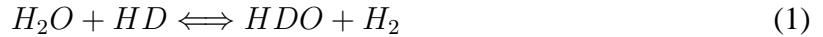
Protium (^1H) and deuterium (^2H or D) are the only two stable isotopes of hydrogen. The largest mass difference between two isotopes of any element leads to rather distinct properties of hydrogen isotopologues (for example HDO and H_2O). Differences in boiling point, vapour pressure and reactivity of compounds with different isotopes will result in their having unique natural abundances. Once formed, a process of isotopic fractionation (resulting from the different physical properties of the two isotopes) can lead to the physical separation of isotopologues through evaporation, condensation, melting or diffusion. The D/H ratio has therefore long been considered to be a useful diagnostic of the geological history of rock formations, bodies of fluid and organic materials.

Deuterium formed during the Big Bang is subsequently destroyed in stars, and therefore its abundance in the interstellar medium decreases with time. Currently, the D/H ratio in the local interstellar medium is of the order of 15×10^{-6} [18], while the initial value, immediately after the big bang, may well have been as high as 30×10^{-6} [19]. The D/H ratio in the protostellar solar nebula has been estimated using measurements of D/H in the atmospheres of Jupiter and Saturn, because HD does not fractionate during the transition from the molecular to metallic form. Observations from the Galileo probe mass spectrometer provide a D/H value

of 26×10^{-6} [20].

Elsewhere in the Solar system, however, the situation is far from this clear cut. The D/H values measured for a variety of Solar system objects vary significantly. The D/H of Vienna Standard Mean Ocean Water (V-SMOW) is 156×10^{-6} , whilst comets 1P/Halley [21], C/1996 B2 Hyakutake [22], C/1995 O1 Hale-Bopp [23] and 8P/Tuttle [24] are enriched in deuterium by a factor of between 1.5 and three times that value.

The enrichment of deuterium in water over that observed in H_2 is a direct result of equilibrium chemistry in the outer regions of the proto-planetary disk. In that disk, the isotopic fractionation of deuterium in water and deuterated hydrogen was governed by the reversible reaction shown in the following equation [16]:



At low temperatures, the sequestration of deuterium in water is favoured over its emplacement in deuterated hydrogen, and so there is a gradual enrichment of deuterium in water as a function of time. At greater heliocentric distances, it has been shown that the relative enrichment of deuterium in water is significantly greater than at small heliocentric distances, resulting in the model distribution of the variation in the deuteration of water compared to that in deuterated hydrogen shown in Figure 1.

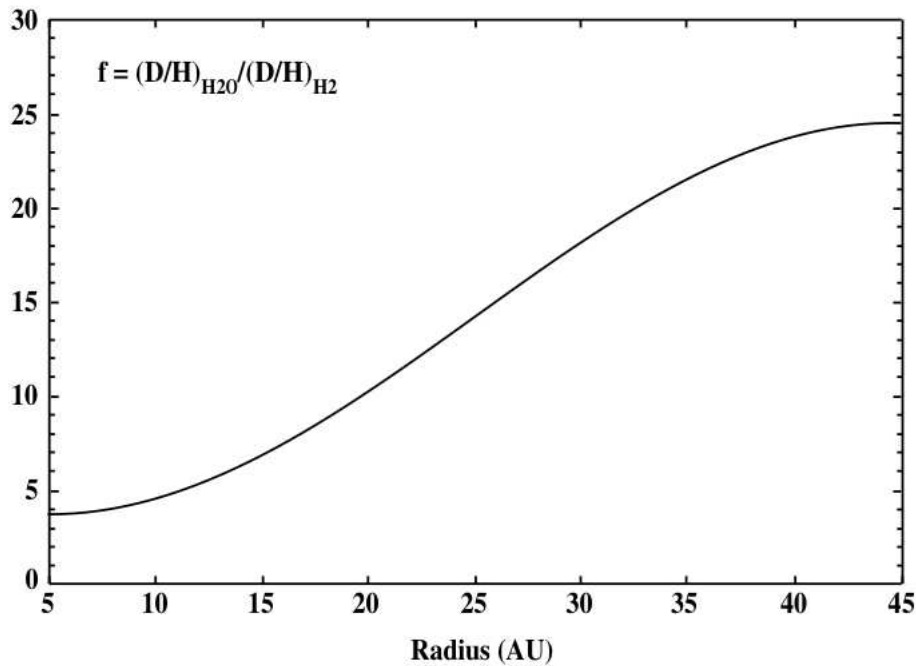


Fig. 1: The variation in the ratio of the deuteration in water to that in deuterated hydrogen, as a function of heliocentric distance, in the proto-planetary disk, taken from [16]. This illustrates how the deuteration of the volatiles incorporated into objects that formed beyond the ice-line will have been a strong function of their formation location.

By contrast, the deuteration levels measured in meteorites are far closer to that measured in the Earth's oceans (see e.g. Fig. 1 of [25]). That similarity has been used to suggest that

the bulk of the Earth's water was delivered by asteroidal, rather than cometary bodies² - with [26] suggesting that, if the carbonaceous chondrites were the main source of oceanic water, another suggested source (the comets) could have contributed only a small fraction (less than 10%). Following this logic, it has often been assumed that the initial volatile budget of all the terrestrial planets would have been identical to that of the Earth, although [27] showed that the terrestrial planets would have experienced significantly different contributions of volatiles from cometary and asteroidal bodies.

A number of studies (e.g. [25, 28, 16]) have suggested that the D/H ratio within ices accreted in the outer Solar system should vary significantly as a function of heliocentric distance within the Solar nebula. The lowest D/H ratios would be found in objects which accreted near the ice-line, the innermost location where water could condense as a solid, and the largest D/H ratios would be found in volatiles that condensed beyond the current orbit of Neptune. Figure 1 shows the predicted enrichment in D/H for water over that in deuterated hydrogen as a function of heliocentric distance in the outer Solar system. It is clear that objects that formed at different heliocentric distances would have incorporated volatiles containing vastly different amounts of deuterium. The less stirred the disk, the more pronounced the variation in D/H as a function of heliocentric distance would be between one body and the next (since increased stirring would doubtless bring icy bodies with high deuteration to the inner reaches of the nebula). It is highly likely that the bulk of volatile material accreted by a given object would be sourced from its immediate surroundings, however, and so measurements of the deuteration of objects in the outer Solar system give us a tool by which their formation location can be constrained.

Origin of CH₄ in the atmosphere of Titan

In 1981, Prinn and Fegley [30] assumed that, in the primordial solar nebula, carbon and nitrogen were entirely sequestered in CO and N₂. During the early stages of Saturn's formation, a dense and warm sub-nebula developed, which enabled the conversion of CO to CH₄ and N₂ into NH₃. This methane and ammonia was accreted to form icy planetesimals, the building blocks of Titan. By contrast, Mousis et al. [31] argued that such conversion of CO and N₂ into methane and ammonia is unlikely to occur in conditions that would have been prevalent in the Saturn sub-nebula, and that therefore CH₄ would have to be present in the primary solar nebula in order to explain its accretion onto Titan.

According to the first model, methane becomes enriched in deuterium gradually when CH₃D in vapour phase exchanges deuterium with hydrogen. After the temperature drops below 200K, this process stops, but isotopic fractionation can continue through solar photolysis and outgassing processes.

The model put forward by Mousis et al. instead assumed that vaporisation of CH₄ happened during the infall of icy planetesimals onto the protoplanetary disk, which allowed the exchange of deuterium with hydrogen from the solar nebula. Methane was later released from the subsurface layers to the atmosphere of Titan. The D/H ratio predicted from this model is in good agreement with measurements without requiring additional fractionation

²The origin of the Earth's water has long been debated, with most modern theories favouring an exogenous source of our planet's oceans. We direct the interested reader to section 4, "Planetary Features" of [29], and references therein, for a detailed discussion of the origin of Earth's water.

to have occurred. Since methane undergoes solar photolysis by breaking into hydrocarbons, cryovolcanism was proposed as its replenishment mechanism.

More recently Atreya et al. [32] have suggested that so-called “serpentinization” reactions (i.e. hydrothermal reactions between silicates and water) in the interior of Titan could generate CH_4 . However, Mousis et al. [33] point out that this is unlikely because it would imply a relatively low value for the D/H of the water involved (similar to the V-SMOW value). They argue that water ice delivered to Titan should have a higher D/H, similar to that measured in comets, and in the Enceladus plume [34] and that a primordial origin for Titan’s methane is more likely.

D/H ratio measurements in Titan’s atmosphere

Two methods were used to determine the D/H ratio in Titan’s atmosphere. In-situ measurements were taken by the Cassini-Huygens probe [35], and used the abundance of molecular and deuterated hydrogen measured by the gas chromatograph mass spectrometer carried on-board, yielding a D/H ratio of $(135 \pm 30) \times 10^{-6}$ for the satellite’s atmosphere.

Measurements of the D/H ratio can also be obtained using remote sensing observations of the spectrum of Titan from the Cassini spacecraft and ground-based telescopes. These observations are analysed using radiative transfer models, such as the VSTAR model described in [36]. Along with molecular nitrogen, which is the most abundant gas in Titan’s atmosphere, methane is a major component, comprising a few percent of the atmosphere, as measured by mole fraction. The spectrum of methane has four vibrational modes forming overlapping absorption bands in the infrared region, which become increasingly complex towards higher energies. Measurements of Titan’s D/H ratio from observations in the thermal infrared with the Cassini CIRS instrument give a value of $(159 \pm 33) \times 10^{-6}$ [37]

New, improved laboratory measurements of methane lines in the near infrared at temperatures relevant to cold regions of the Solar system are now becoming available for use in radiative transfer models [2]. These line lists can be used to model spectra of Titan observed with near infrared spectrometers on ground-based telescopes. The model shown in Figure 2 yields a D/H ratio of $(143 \pm 16) \times 10^{-6}$ [1] for the atmosphere of Titan. De Bergh et al. [38] used a different set of data from KPNO/FTS with the improved list of methane lines from [39], and obtained a rather different result $(113 \pm 25) \times 10^{-6}$. It is becoming clear that a number of different datasets have to be analysed and modelled to resolve the differences between estimates obtained from different methods.

Modelling of the 1.58 μm window of Titan’s atmosphere

We obtained spectra of Titan in the J, H and K bands (1.1 to 2.4 μm) with the Near-Infrared Integral Field Spectrometer (NIFS) on the Gemini North 8m telescope. The NIFS spectrum in the 1.53 to 1.59 μm region and its VSTAR model are reproduced from [1] in Figure 2, where data and model are shown in the top panel. In the second panel from the top, the residuals are plotted between the data and the model, which includes only CH_4 features. In the panel below, the absorption from the CH_3D are added, while in the bottom panel the addition of CO 3-0 lines based on a mixing ratio of 50 ppmv completes the removal of unaccounted

residuals from this CO band. The details of the modelling techniques are described in [40] and the parameters of the final model are presented in Table 2 of [1].

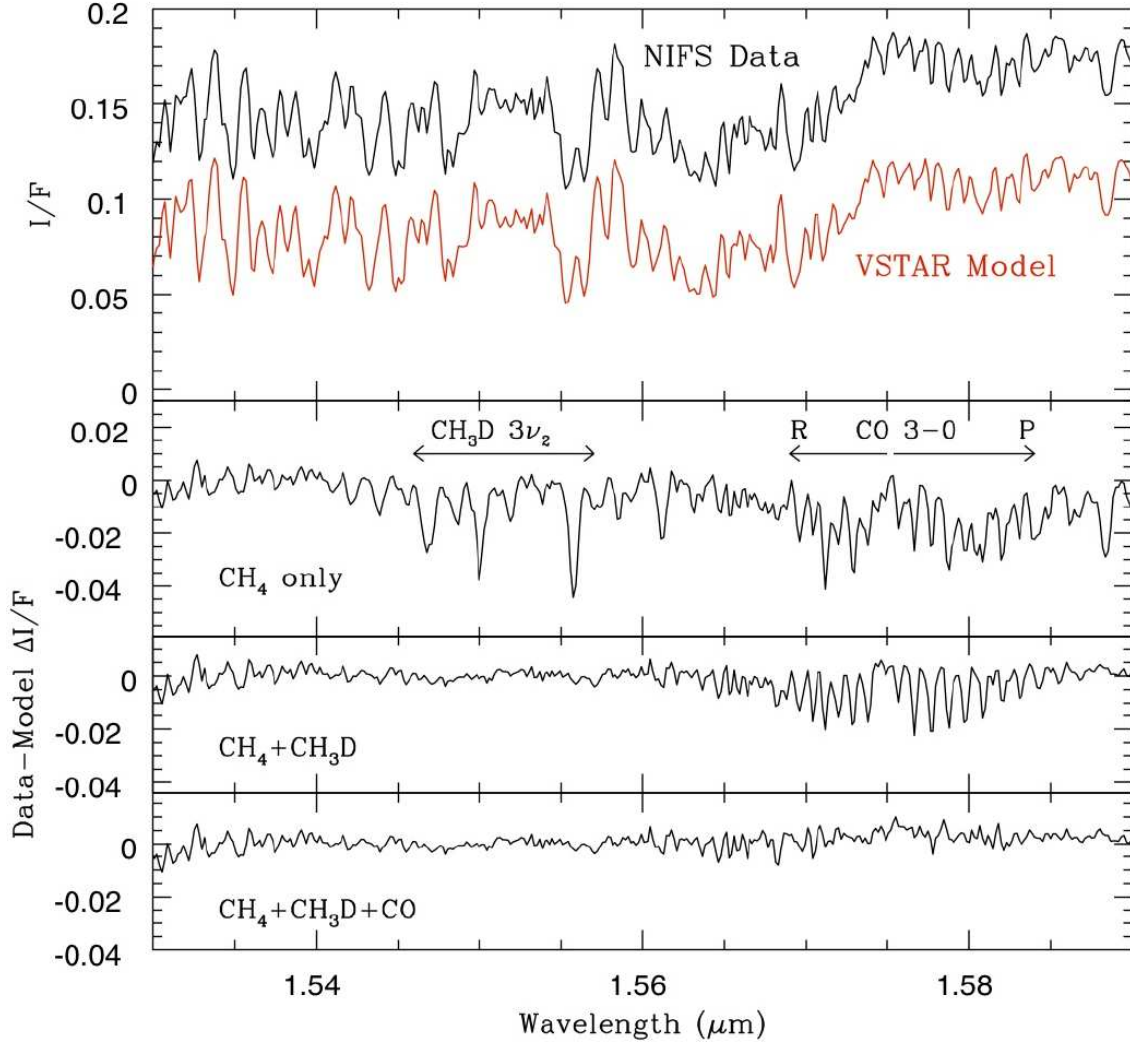


Fig. 2: NIFS spectrum in H-band region of the CH_3D absorptions compared with the VSTAR model (top panel). The residuals in panels below are described in more detail in the text and in [1].

As discussed in the previous section, the accuracy of the D/H measurements obtained from the near IR ground-based observations with NIFS is significantly higher than that of the in-situ Huygens probe measurements, or of the Cassini spacecraft results. An important advantage of ground-based observing is the ability to obtain spectra at higher resolution than that of space instruments. We are therefore pursuing a program of observation of Titan and the methane-rich giant planets in the Solar system with even higher resolution than the $R \sim 5000$ of the NIFS observations. The aim is to use the high-resolution spectra in conjunction with the latest methane spectral line data to measure D/H for all these objects as accurately as is possible.

In June 2011 we observed Titan with the Gemini Near Infra-Red Spectrometer (GNIRS) on the Gemini North 8m telescope, which allowed spectroscopy with the increased resolving

power of $R \sim 18000$. The data were reduced by using the Gemini IRAF GNIRS package. We removed the solar and telluric features resulting from the Earth's atmosphere by dividing the extracted Titan spectra by the spectrum of a G-type standard star, which was observed immediately after or before the target object. We used the same model of Titan's atmosphere adopted for the low resolution NIFS spectrum, with adjustments in albedo and atmospheric opacity parameters, which are subject to seasonal changes. The D/H ratio was fixed at the level derived in [1]. The observed GNIRS spectrum is shown in Figures 3 and 4 in black with the VSTAR model overplotted in red. The region corresponding to that shown in Figure 2, which contains the absorption due to the $3\nu_2$ band of CH_3D , is visible in Figure 4. Although there is a close agreement between our data and model, the match of the features present in both spectra can be improved, as suggested by new modelling of this region undertaken by Campargue et al. [2]. We are currently exploring the sensitivity of this result to refinements in additional parameters, such as changes in methane mixing ratio in Titan's lower atmosphere.

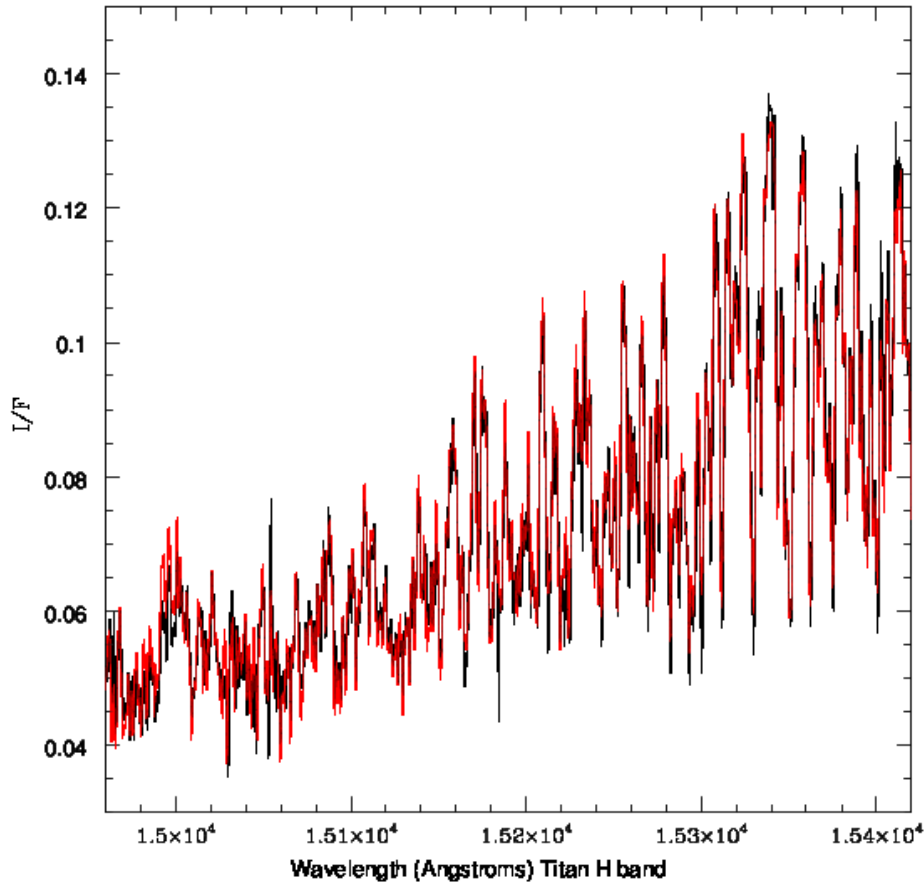


Fig. 3: GNIRS spectrum of Titan reflectance (I/F) plotted in black with the VSTAR model overlaid in red.

Discussion and conclusions

In this work, we detail the progress of our investigations into the D/H ratio contained within objects in the outer regions of the Solar system. Here, we have concentrated on the deuteration

of methane in the atmosphere of Saturn's largest satellite, Titan. Two different models exist that attempt to explain the origin of methane in the primordial Titan. Both models feature the progressive enrichment of deuterium in methane in the Solar nebula - and therefore predict that the level of deuteration in Titan's atmosphere will depend on the heliocentric distance at which the planetesimals incorporated into Titan formed, along with any subsequent processing that they experienced in the circum-Saturnian disk and further processing over the course of Titan's life.

Both models for the origin of Titan's methane argue that the ongoing enrichment of deuterium in methane would be far slower once the local temperature fell below 200K, suggesting that the bulk of processing experienced by the methane likely happened in the proto-planetary disk, prior to Titan's formation. As such, the Titanian D/H ratio is almost certainly strongly diagnostic of its true formation location, and therefore a strong indication of the formation location of Saturn itself. That, in turn, will provide an important datum for studies that are attempting to dynamically reconstruct the migration of the giant planets by considering their influence on the various small body reservoirs observed in the outer Solar system (e.g. [11, 15]). If Saturn formed at its current location of 9.5 AU from the Sun, and Titan accreted out of the icy planetesimals around this area, the expected deuterium enrichment

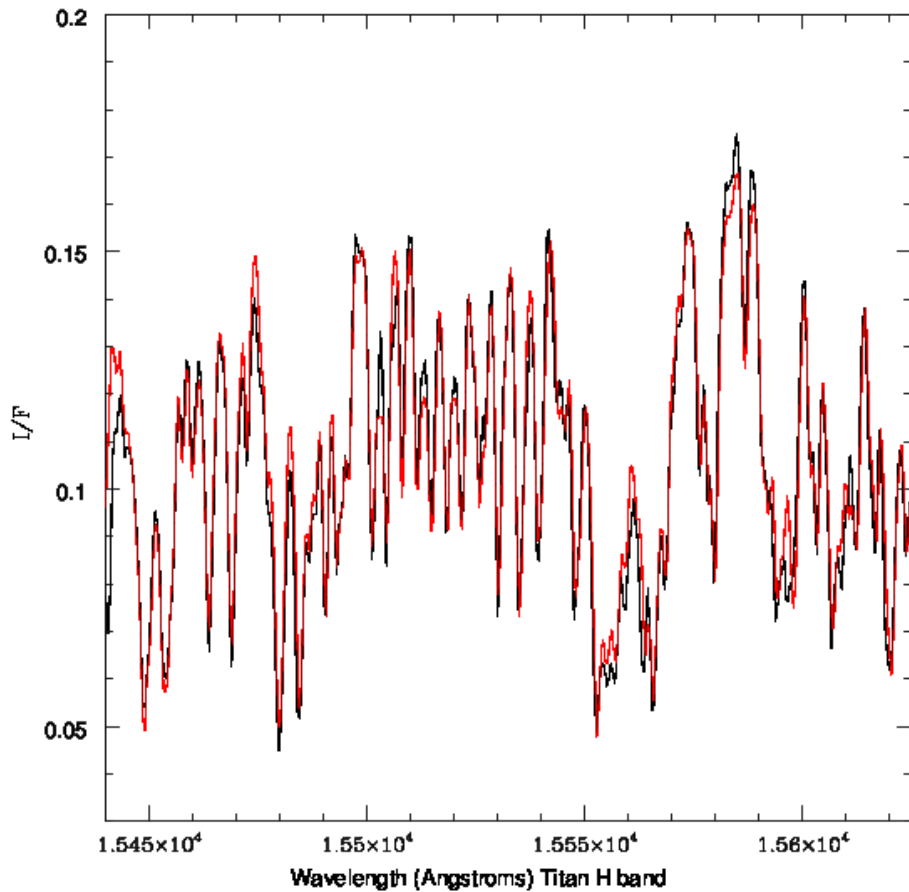


Fig. 4: GNIRS spectrum of Titan (black) coinciding with the region of lower resolution NIFS spectrum from Figure 2. VSTAR model is overlaid in red.

factor in Titan f would be of the order of 5 times the initial proto-solar value (see figure 1). If the value of 26×10^{-6} obtained for Jupiter [20] is representative of the protosolar value we predict $\sim 130 \times 10^{-6}$ for an object formed at this location. The value $(143 \pm 16) \times 10^{-6}$ obtained from the NIFS data [1] is consistent with this scenario. However, more accurate measurements would help to further constrain the formation location and mechanism.

We are currently in the process of analysing data obtained using higher resolution GNIRS for the four giant planets (Jupiter, Saturn, Uranus and Neptune) in the H and K bands. We intend to apply a similar modelling technique as presented in this work to derive accurate D/H values for each of those planets in turn. We will also use our GNIRS observations for the K-band $2\mu\text{m}$ regions to measure the D/H ratio from the CH_3D absorption due to the $\nu_5 + 3\nu_6$ and $2\nu_3 + 2\nu_6$ bands, which were detected in Titan's NIFS spectrum (as presented in [40]). However the detailed modelling of this region is dependent on availability of intensities in these bands, which still await laboratory measurement.

It seems likely that the D/H ratio in the atmospheres of Jupiter and Saturn will be strongly influenced by their accretion of hydrogen and deuterated hydrogen directly from the proto-planetary nebula, and therefore they might be expected to display values similar to the Solar value (since only a small fraction of their hydrogen will have been accreted in the form of solid volatile material such as water and methane). By contrast, the hydrogen/deuterium budget of Uranus and Neptune was most likely primarily accreted in the form of solids - such as water, methane and ammonia. The deuteration of these planets, then, will likely strongly reflect the accretion location of their volatile budgets - and therefore, the location at which those planets accreted the bulk of their mass. The situation is perhaps even more clear cut for the regular satellites of the giant planets (such as Titan), whose volatile budget will have been accreted entirely in the form of solid planetesimals. However, it is possible that the volatiles accreted to these bodies underwent further processing in circum-planetary disks around their host planet prior to accreting to form the satellites we observe today.

Our future studies of deuteration in the outer Solar system will help to answer a variety of outstanding questions on the formation and evolution of our Solar system, and, taken in concert with independent dynamical tests of planetary migration, should allow us to finally determine the true architecture of our Solar system *prior to the migration of its giant planets*.

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References

- [1] Bailey, J., "Methane and Deuterium in Titan's Atmosphere", *Proceedings of the 11th Australian Space Science Conference*, 2012, Vol. 55, 64 - 76
- [2] Campargue, A., Wang, L., Mondelain, D., Kassi, S. et al., "An empirical line list for methane in the 1.26-1.71 μm region for planetary investigations ($T = 80\text{-}300\text{ K}$). Application to Titan", *Icarus*, Vol. 219, 2012, 110
- [3] Lyttleton, R. A., "The Origin of the Solar System" *Monthly Notices of the Royal Astronomical Society* Vol. 9 , 1936, 559
- [4] Woolfson, M. M. "A Capture Theory of the Origin of the Solar System" *Proceedings of the Royal Society of London. Series A, Mathematical and Physical Sciences*, Volume 282, Issue 1391, 1964, pp. 485-507
- [5] Lissauer, J. J. "Planet formation" *Annual Review of Astronomy and Astrophysics* Vol. 31, 1993, pp. 129 - 174
- [6] Mayor, M. and Queloz, D. "A Jupiter-mass companion to a solar-type star" *Nature* Vol. 378, 1995, pp. 355 - 359
- [7] Malhotra, R. "The origin of Pluto's peculiar orbit" *Nature* Vol. 365, Issue 6449, 1993, pp. 819 - 821
- [8] Malhotra, R. "The Origin of Pluto's Orbit: Implications for the Solar System Beyond Neptune" *Astronomical Journal* Vol. 110, 1995, p. 420
- [9] Gomes, R., Levison, H. F., Tsiganis, K. and Morbidelli, A. "Origin of the cataclysmic Late Heavy Bombardment period of the terrestrial planets" *Nature*, Vol. 435, Issue 7041, 2005, pp. 466-469
- [10] Morbidelli, A., Levison, H. F., Tsiganis, K. and Gomes, R. "Chaotic capture of Jupiter's Trojan asteroids in the early Solar system" *Nature*, Vol. 435, Issue 7041, 2005, pp. 462 - 465
- [11] Lykawka, P. S., Horner, J., Jones, B. W. and Mukai, T. "Origin and dynamical evolution of Neptune Trojans - I. Formation and planetary migration" *Monthly Notices of the Royal Astronomical Society* Vol. 398, 2009, pp. 1715 - 1729
- [12] Lykawka, P. S., Horner, J., Jones, B. W. and Mukai, T. "Formation and dynamical evolution of the Neptune Trojans - the influence of the initial Solar system architecture" *Monthly Notices of the Royal Astronomical Society* Vol.. 404, Issue 3, 2010, pp. 1272-1280
- [13] Thommes, E. W., Duncan, M. J. and Levison, H. F. "The Formation of Uranus and Neptune among Jupiter and Saturn" *The Astronomical Journal* Vol 123, Issue 5, 2002, pp. 2862 - 2883
- [14] Lykawka, P. S. and Horner, J. "The capture of Trojan asteroids by the giant planets during planetary migration" *Monthly Notices of the Royal Astronomical Society* Vol. 405, Issue 2, 2010, pp. 1375 - 1383
- [15] Horner, J., Koch, F. E. and Lykawka, P. S. "Capturing Trojans and Irregular Satellites - the key required to unlock planetary migration" *Proceedings of the 12th Annual Australian Space Science Conference*, 2013, submitted
- [16] Horner, J., Mousis, O. and Hersant, F. "Constraints on the Formation Regions of Comets from their D:H ratios" *Earth, Moon and Planets*, Vol. 100, Issue 1-2, 2007, pp. 43 - 56
- [17] Horner, J., Mousis, O., Alibert, Y., Lunine, J. I. and Blanc, M. "Constraints from deuterium on the formation of icy bodies in the Jovian system and beyond" *Planetary and Space Science*, Vol. 56, Issue 2, 2008, pp. 1585 - 1595
- [18] McCullough, P., "The interstellar deuterium-to-hydrogen ratio - A reevaluation of Lyman absorption-line measurements", *ApJ* Vol. 390, 1992, 213-218

- [19] Noterdaeme, P. Lopez, S., Dumont, V., Ledoux, C., Molaro, P. and Petitjean, P., "Deuterium at high-redshift: Primordial abundance in the $z_{abs} = 2.621$ damped Ly-alpha system towards CTQ247", *A&A*, vol. 542, 2012, L33
- [20] Mahaffy, P.R., Donahue, T. M., Atreya, S.K., Owen, T.C. and Niemann, H.B. "Galileo Probe Measurements of D/H and $^3\text{He}/^4\text{He}$ in Jupiter's Atmosphere", *Space Science Reviews*, 1998, Volume 84, pp. 251-263
- [21] Eberhardt, P., Reber, M., Krankowsky, D. and Hodges, R. R. "The D/H and $^{18}\text{O}/^{16}\text{O}$ ratios in water from comet P/Halley." *Astronomy & Astrophysics* Vol. 302, 1995, p. 301
- [22] Bockelee-Morvan, D., Gautier, D., Lis, D. C., Young, K., Keene, J., Phillips, T., Owen, T., Crovisier, J., Goldsmith, P. F., Bergin, E. A., Depois, D. and Wootten, A. "Deuterated Water in Comet C/1996 B2 (Hyakutake) and Its Implications for the Origin of Comets" *Icarus*, Vol. 133, Issue 1, 1998, pp. 147 - 162
- [23] Meier, R., Owen, T. C., Matthews, H. E., Jewitt, D. C., Bockelee-Morvan, D., Biver, N., Crovisier, J. and Gautier, D. "A Determination of the HDO/H₂O Ratio in Comet C/1995 O1 (Hale-Bopp)" *Science* Vol. 279, 1998, p. 842
- [24] Villanueva, G. L., Mumma, M. J., Bonev, B. P., DiSanti, M. A., Gibb, E. L., Bönnhardt, H. and Lippi, M. "A sensitive search for deuterated water in comet 8P/Tuttle" *The Astrophysical Journal* Vol 690, 2009, pp. L5 - L9
- [25] Drouart, A., Dubrulle, B., Gautier, D. and Robert, F. "Structure and transport in the solar nebula from constraints on deuterium enrichment and giant planets formation." *Icarus*, Vol. 140, 1999, pp. 129 - 155
- [26] Robert, F., Gautier, D. and Dubrulle, B. , "The Solar System D/H Ratio: Observations and Theories", *Space Science Review* Vol. 92, 2000, 201-224
- [27] Horner, J., Mousis, O., Petit, J.-M. and Jones, B. W. "Differences between the impact regimes of the terrestrial planets: Implications for primordial D:H ratios" *Planetary and Space Science*, Vol. 57, Issue 12, 2009, pp. 1338 - 1345
- [28] Mousis, O., Gautier, D., Bockelee-Morvan, D., Robert, F., Dubrulle, B. and Drouart, A. "Constraints on the Formation of Comets from D/H Ratios Measured in H₂O and HCN" *Icarus*, Vol. 148, 2000, pp. 513 - 525
- [29] Horner, J. and Jones, B. W. "Determining habitability: which exoEarths should we search for life?" *International Journal of Astrobiology*, Vol. 9, 2010, pp. 273 - 291
- [30] Prinn, R. G. and Fegley B., "Kinetic inhibition of CO and N₂ reduction in circumplanetary nebulae - Implications for satellite composition", *Astrophysical Journal*, Vol. 249, 1981, 308-317
- [31] Mousis, O., Gautier, D. and Coustenis, A., "The D/H Ratio in Methane in Titan: Origin and History", *Icarus*, Vol 159, 2002, 156-165
- [32] Atreya, S.K., Adams, E.Y., Niemann, H.S., Demick-Montelara, J.E., Owen, T.C., Fulchigoni, M., Francesca, F., Wilson, E.H., "Titan's Methane Cycle", *Plan. Space Sci.*, Vol. 54, 2006, pp. 1177-1187.
- [33] Mousis, O., Lunine, J.I., Pasek, M., Cordier, D., Waite, J.H., Mandt, K.E., Lewis, W.S., Nguyen, M.-J., "A primordial origin for the atmospheric methane of Saturn's moon Titan", *Icarus*, Vol 204, 2009, pp. 749-751.
- [34] Waite, J.H., et al., "Liquid water on Enceladus from observations of ammonia and ^{40}Ar in the plume", *Nature*, Vol 460, 2009, pp. 487-490.
- [35] Niemann, H.B., Atreya, S. K., Demick, J. E, Gautier, D., Haberman, J. A., Harpold, D. N., Kasprzak, W. T., Lunine, J. I., Owen, T. C. and Raulin, F., "Composition of Titan's lower atmosphere and simple surface volatiles as measured by the Cassini-Huygens probe gas chromatograph mass spectrometer experiment", *Journal of Geophysical Research*, Vol. 115, 2010, Issue E12

- [36] Bailey J. and Kedziora-Chudczer, L., “Modelling the spectra of planets, brown dwarfs and stars using VSTAR”, *MNRAS*, Vol. 419, 2012, 1913-1929
- [37] Nixon, C.A. et al., “Isotopic Ratios in Titan’s Methane: Measurements and Modeling”, *Astrophysical Journal*, Vol. 749, 2012, 159.
- [38] de Bergh, C., Courtin, R., Bzard, B., Coustenis, A. et al., “Applications of a new set of methane line parameters to the modeling of Titan’s spectrum in the 1.58 μm window”, *Planetary and Space Science* Vol. 61, 2012, 85-98
- [39] Wang L, Kassi S, Liu A. W., Hu S.M. and Campargue A. , “The 1.58 μm transparency window of methane (6165-6750 cm^{-1}): Empirical line list and temperature dependence between 80 and 296 K”, *Journal of Quantitative Spectroscopy & Radiative Transfer*, Vol. 112, 2011, 937-951
- [40] Bailey, J., Ahlsved, L. and Meadows, V. S., “The near-IR spectrum of Titan modeled with an improved methane line list”, *Icarus*, Vol. 213, 2011, 218 -232